HANKARD

BOSTON UNIVERSITY

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Thesis

AN EXAMINATION OF THE METASTABLE REGION OF THE SYSTEM LITHIUM NITRATE-AMMONIUM NITRATE

by

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HISTORICAL INTRODUCTION

In 1919 Early and Lowry[#1] undertook a study of the cooling curve of Ammonium Nitrate and noted a break in the curve at 122°C indicating a transition from Ammonium Nitrate 1 to Ammonium Nitrate 11.

Five years later Perman and Harrison[#2] undertook a study of the phase relations of the system Lithium Nitrate - Ammonium Nitrate and obtained a two-branched curve with a eutectic at 97°C and 25% Lithium Nitrate (Figure 3). A break was noted in the left (or Ammonium Nitrate) branch at 122°C confirming the earlier work of Early and Lowry. No break was noted in the right hand (or Lithium Nitrate) branch or in a cooling curve run on pure Lithium Nitrate, therefore the existence of only one crystalline modification of that salt was indicated.

In 1942 A. N. Campbell,[#3] using a refined technique, repeated the work of Perman and Harrison and entirely confirmed their results.

In 1945 E. O. Holmes and E. O'Connell[#4] redetermined the phase diagram of the system up to 62% Lithium Nitrate where decomposition invalidated results. Their results not only confirmed the data of Perman and Harrison with a eutectic at 97°C and 25% Lithium Nitrate, but also indicated a second eutectic at 79.5°C and 24.21% Lithium Nitrate (Figure 3).

On the basis of the procedures used to obtain this new eutectic it was suggested that the presence of moisture catalyzed the transition of

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[#1] Early and Lowry	J. Chem. Soc.	115, 1387	(1919)
[#2] Perman and Harrison	J. Chem. Soc.	125, 1709-13	(1924)
[#3] A. N. Campbell	J. Am. Chem. Soc.	64, 2680	(1942)
[#4] Thesis E. O'Connell	378.744BO	AM	(1946)OC

Ammonium Nitrate 1 to Ammonium Nitrate 11 and that the data of Perman and Harrison represented the eutectic point of Ammonium Nitrate 11 and Lithium Nitrate, while the new data represented the eutectic point of Ammonium Nitrate 1 and Lithium Nitrate.

PURPOSE OF PRESENT INVESTIGATION OF THE SYSTEM

The present examination of the system was undertaken in order to further investigate the region 23% to 28% Lithium Nitrate wherein Holmes and O'Connell consistently obtained 90.4°C as the temperature at which the first crystals appeared on the Ammonium Nitrate 11 curve.

DESCRIPTION OF THE EQUIPMENT USED

The thermometer used in the work was a 24 inch, 0.2°, 0-200°C, 76 millimeter immersion type. It was calibrated by comparison with the boiling and melting points of certain pure organic compounds (Appendix I) and the calibrations were applied to all the readings. No stem correction was calculated since all observed transition and eutectic temperatures were converted to correct values by reference to a calibration curve (Figure 4).

The oil used in all runs in the melting point bath was a silica base oil, Dow-Corning Fluid #50 (Viscosity at 25 degrees -- 75 cstks, manufactured by Dow-Corning Corporation, Midland, Michigan.)

The cooling curve apparatus used in all determinations was similar in design to that used by Holmes and O'Connell [#4] with the exception of the replacement of the six inch test tube by an eight inch side arm test tube connection to a source of dry nitrogen.

The source of dry nitrogen was a gas drying train consisting of two wash towers of concentrated sulfuric acid, two large U-tubes of anhydrone and a tank of water pumped nitrogen. The source was set up so as to furnish nitrogen thru an arrangement of stopcocks either to the vacuum system or to the eight inch side-arm test tube in the cooling curve apparatus.

The vacuum system consisted of a MacLeod gauge, moisture trap, mercury pump, and backing pump set up in the conventional manner. It was connected to a specially designed drier in which the samples to be dried were placed.

The special drier consisted of two separate containers of identical design connected to the vacuum line. Each container was used to dry one of the salts used in the work and was labelled with the name of that salt. The design of the container may be seen by referring to Figure 1. It consisted of three separate parts A, B, and C. Part C was sealed into the vacuum system and was the section into which the sample to be dried was placed. Part b was capable of being tightly affixed to Part C by means of a standard taper joint coated with high vacuum grease. And finally Part A could be similarly affixed to B. (Figure 2)

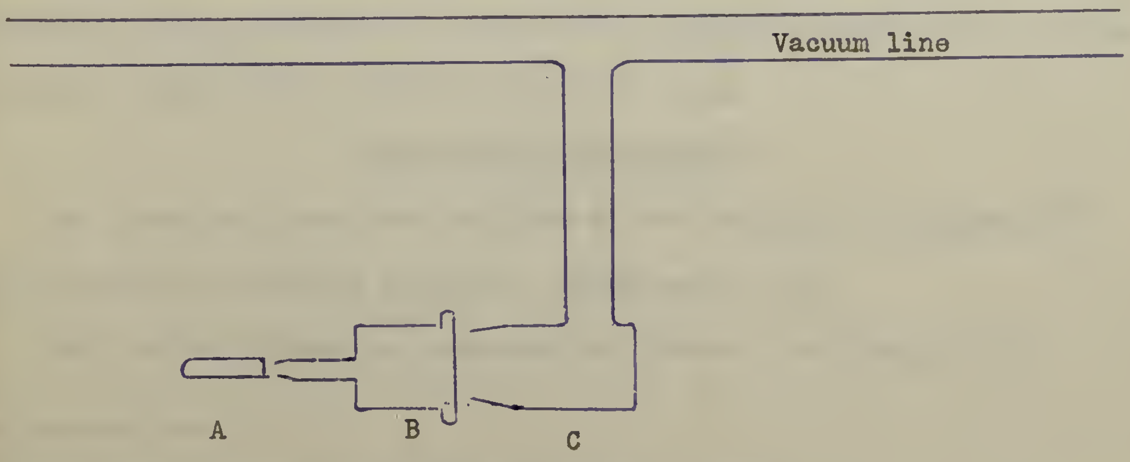

FIGURE 1. Drier assembly

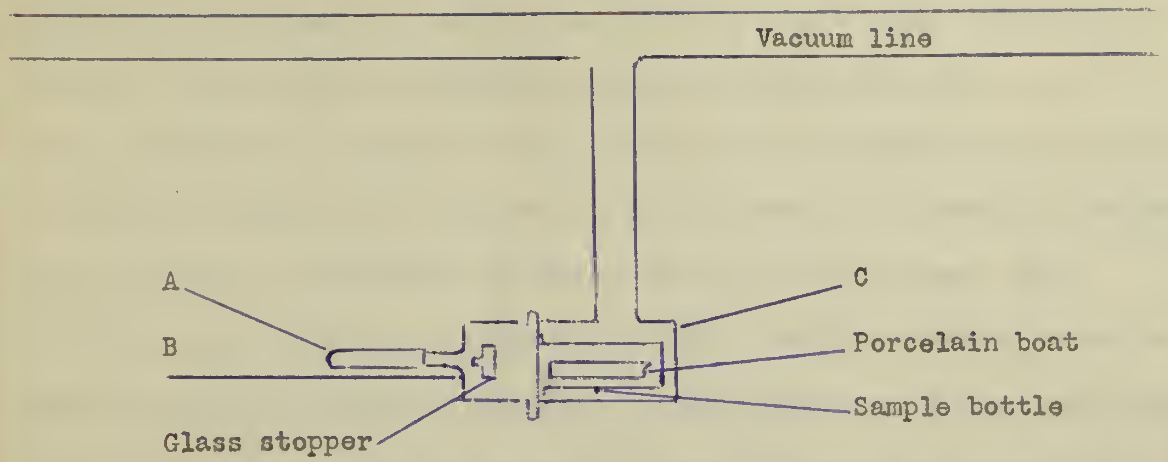

FIGURE 2. Drier in operation

Another group of equipment consisted of special sample bottles into which the porcelain boats containing the samples were placed during the drying process and afterwards during the weighing process. These sample bottles were fitted with glass stoppers which could be readily inserted into the neck of the bottles while they were still in the drier by means of a glass rod inserted into the mouth of part B of the drier (Figure 2).

The apparatus used in the analysis of the dried sample for the presence of nitrogen was a macro Kjeldahl set-up consisting of a 500cc Erlenmeyer flask connected to a trap and a condensor dipping into a 125cc Erlenmeyer flask of 0.1 normal hydrochloric acid.

PURIFICATION OF REAGENTS

The Ammonium Nitrate was supplied by the Committee on Eutectics[#5] and on analysis contained 100.01% of Ammonium Nitrate.

The Lithium Nitrate was converted to Lithium Carbonate by the

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[#5] Committee on Eutectics, National Research Council.

addition of an excess of Ammonium Carbonate to a saturated solution of that salt and heating to insure completeness of precipitation of the Lithium Carbonate. After washing, the Lithium Carbonate was reconverted to Lithium Nitrate by the addition of such an amount of freshly distilled Nitric Acid that the Lithium Carbonate was not all dissolved. The Lithium Nitrate crystals were then filtered by suction, washed, spread on a watch glass and dried in a dessicator over Anhydrone. During the period of experimentation the crystals were frequently ground to insure drying.

EXPERIMENTAL PROCEDURE

(a) The vacuum drying technique: A porcelain boat of known weight was filled with finely ground Ammonium Nitrate, weighed, and placed at once into a stoppered sample bottle. A second boat of known weight was filled with enough finely ground Lithium Nitrate to approximate the percentage of Lithium Nitrate required in the determination and also placed immediately into a stoppered sample bottle. The sample bottles were next placed into their respective sections of the drier (C in Figure 1), the ground glass stoppers of the bottles were removed and placed in Section B in position to be inserted into the bottles, parts A, B, and C were joined under a coat of high vacuum grease, and finally the drier was placed under vacuum. After drying for 24 hours under a pressure of 0.001 millimeters of mercury, dry nitrogen was passed into the drier and by removal of section A the ground glass stoppers were pushed forward into the sample bottles. At once section B was disconnected, the samples reground and subjected to another 24 hour period of drying. When the drying was completed the samples were removed as before and weighed in the sealed

sample bottles. After weighing, the dried samples were removed separately from the sample bottles and quickly deposited in the eight inch side-arm test tube thru which dry nitrogen was passing. The porcelain boats were placed in their respective sample bottles, the bottles reweighed, and the weight of the samples determined by difference.

(b) The cooling curve technique: The side-arm test tube was at once placed into a bath of hot oil and the temperature raised with stirring until the mixture of Ammonium and Lithium Nitrate completely melted. After melting, which in this experiment occurred between 125-135°C, the mixture was cooled with frequent agitation at a rate of 0.5° per minute with readings being taken every two minutes until the appearance of the first crystal and at one minute intervals thereafter. The temperature of appearance of the first crystal and also of the eutectic point were carefully noted. Repetitions were made until both the temperature of appearance of the first crystal and of the eutectic point checked to 0.1°C.

TABLE 1.

TRANSITION AND EUTECTIC POINTS OBTAINED WITH IMPURE LITHIUM NITRATE

% BY WT. $LiNO_3$	OBS.TRANS. DEG.C	CORR. S&T	CORR.TRANS. DEG.C	OBS.EUT. DEG.C	CORR. S&T	CORR.EUT. DEG.C
19.7	107.0	+0.1	107.1	90.2	0.0	90.2
20.4	106.8	+0.1	106.9	85.4	0.0	85.4
21.7	103.5	+0.1	103.6	89.4	0.0	89.4
22.6	102.6	+0.1	102.7	----	---	----
25.7	97.8	0.0	97.8	90.9	0.0	90.9
25.8	97.8	0.0	97.8	90.3	0.0	90.3
26.7	94.8	0.0	94.8	89.0	0.0	89.0
26.9	95.0	0.0	95.0	90.6	0.0	90.6
27.7	92.0	0.0	92.0	92.0	0.0	92.0
28.2	91.8	0.0	91.8	91.8	0.0	91.8
29.0	92.5	0.0	92.5	90.7	0.0	90.7
30.4	96.4	0.0	96.4	91.4	0.0	91.4
					AVE:	90.2°C

The results of table 1 deviated so greatly from the expected curve that an impurity was suspected in the Lithium Nitrate. Therefore an analysis for nitrate nitrogen was undertaken in order to establish the purity of that salt. The analytical method, based on Devarda's Method#6, follows:

In this procedure a half gram sample of vacuum dried Lithium Nitrate was introduced into a 500cc Erlenmeyer flask, diluted with 60cc of water, mixed with 5cc of ethyl alcohol, 40cc of potassium hydroxide (Sp.G. 1.3) and 2 grams of Devarda's Alloy, connected to a trap and condensor, heated gently for 30 minutes and finally distilled into a 125cc Erlenmeyer flask containing 30cc of 0.1N hydrochloric acid. The standard acid was back-titrated with standard sodium hydroxide and the per cent of nitrogen determined on the basis of the amount of hydrochloric acid required to neutralize the ammonia liberated in the reaction.

Since the impurity was at first assumed to be water (later results indicated nitric acid as the source of error), the weight of water present was determined by calculating the weight of Lithium Nitrate present on the basis of the per cent of nitrogen found and subtracting this weight of Lithium Nitrate from the sample weight. Finally the per cent of water present was calculated.

The results of several determinations of nitrogen in the impure Lithium Nitrate sample follow in table 2.

#6 Hillebrand and Lundell, "Applied Inorganic Analysis", Tenth printing, John Wiley & Sons Inc., New York, N.Y., 1948, p. 640.

TABLE 2.

PER CENT WATER IN IMPURE $LiNO_3$ SAMPLE (DRIED 48 HRS)

WT. SAMPLE	%N	THEO. %N	DEV.	GM. H_2O	%H_2O
0.4815gm	21.57	20.32	+1.25	----	----
0.5579	21.58	20.32	+1.26	----	----
0.4308	21.36	20.32	+1.04	----	----
0.4619	21.14	20.32	+0.82	----	----
0.4011	21.36	20.32	+1.04	----	----

The results of table 2 indicated an excess of nitrogen over the theoretical in the Lithium Nitrate being used. Furthermore they showed that this nitrogen was present in no fixed amount since check results were obtained only by using an aliquot portion and not from individual samples. Tests on water solutions of the Lithium Nitrate gave a Ph of 5.3 and an acidic reaction to blue litmus and brom cresol purple as contrasted to a Ph of 6.8 and no acidic reaction from the original bottle samples. No test for nitrite was obtained with Potassium Iodide Starch paper. Such results indicated the presence of a small amount of nitric acid in the sample and made necessary a second recrystallization of the Lithium Nitrate. The vacuum dried recrystallized sample gave a Ph of 6.8, no reaction to blue litmus or brom cresol purple, and averaged 20.32% as the amount of nitrate nitrogen present. The results of several determinations of nitrogen in the recrystallized sample follow:

TABLE 3.

PER CENT WATER IN PURE $LiNO_3$ SAMPLE (DRIED 48 HRS)

WT. SAMPLE	%N	THEO. %N	DEV.	GM. H_2O	%H_2O
0.5488gm	20.34	20.32	+0.02	0.00	0.00
0.5488	20.33	20.32	+0.01	0.00	0.00
0.5488	20.31	20.32	-0.01	0.00	0.00
0.5488	20.30	20.32	-0.02	0.00	0.00
0.5081	20.32	20.32	0.00	0.00	0.00

Since the completeness of the drying was established by the results in table 3, a second series of determinations of transition and eutectic points was made using the recrystallized Lithium Nitrate. These results are tabulated in table 4.

TABLE 4

TRANSITION AND EUTECTIC POINTS OBTAINED WITH PURE LITHIUM NITRATE

% BY WT. $LiNO_3$	OBS. TRANS. DEG. C	CORR. S&T	CORR. TRANS. DEG. C	OBS. EUT. DEG. C	CORR. S&T	CORR. EUT. DEG. C
19.7	108.6	+0.1	108.7	90.2	0.0	90.2
24.6	95.0	0.0	95.0	90.8	0.0	90.8
25.2	97.4	0.0	97.4	90.9	0.0	90.9
25.6	94.0	0.0	94.0	90.6	0.0	90.6
26.0	90.5	0.0	90.5	90.2	0.0	90.2
26.5	92.6	0.0	92.6	90.4	0.0	90.4
27.4	93.0	0.0	93.0	89.9	0.0	89.9
27.6	94.9	0.0	94.9	90.6	0.0	90.6
29.0	99.4	+0.1	99.5	89.2	0.0	89.2
31.4	113.0	+0.1	113.1	91.5	0.0	91.5
						AVE: 90.4°C

Using the transition points tabulated in table 4, a phase diagram was constructed for the system Ammonium Nitrate 11 and Lithium Nitrate (Figure 3). The eutectic point in this phase diagram was at 90.4°C and 26% Lithium Nitrate and was evaluated by averaging the eutectic points in table 4.

INTERPRETATION OF RESULTS

The phase diagram of Ammonium Nitrate 11 and Lithium Nitrate has been extended beyond the eutectic point of Perman and Harrison[#2] to a new eutectic at 90.4°C and 26% Lithium Nitrate. No evidence was obtained of a eutectic at 97.0°C and 25% Lithium Nitrate as indicated by Perman and Harrison, A.N.Campbell,[#3] and Holmes and O'Connell[#4].

The left (or Ammonium Nitrate) branch of the phase diagram follows

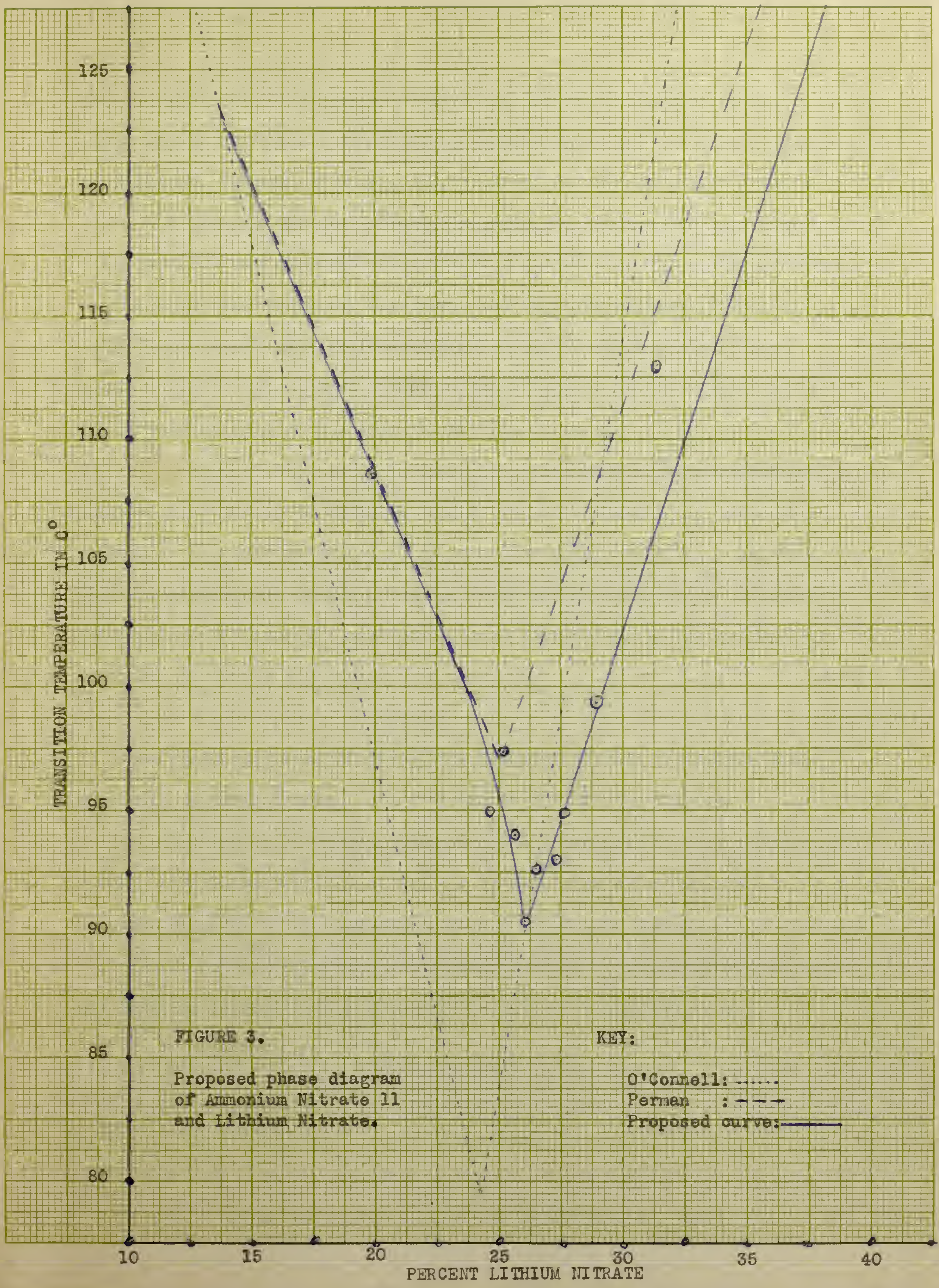

FIGURE 3.

Proposed phase diagram of Ammonium Nitrate 11 and Lithium Nitrate.

the corresponding branch of the Perman and Harrison data down to the point 99.0°C and 24% Lithium Nitrate at which point the curve bends away to intersect the data of Holmes and O'Connell at the new eutectic point of 90.4°C and 26% Lithium Nitrate.The right (or Lithium Nitrate) branch rises from the new eutectic point in the shape of a curve moving parallel to the right hand branch of the Perman and Harrison diagram. It may be noted that the new eutectic temperature of 90.4°C corresponds to the value consistently obtained by Holmes and O'Connell in the region 23% to 28% Lithium Nitrate on the Ammonium Nitrate 11 curve.

No data were obtained to substantiate the Ammonium Nitrate 1-Lithium Nitrate curve indicated by Holmes and O'Connell. Furthermore, since the samples on analysis contained no water and since all cooling curves were run in an atmosphere of dry nitrogen, there was no opportunity to obtain evidence for the possible catalytic action of moisture in the transition of Ammonium Nitrate 1 to Ammonium Nitrate 11.

SUMMARY

The phase relations of the system Ammonium Nitrate 11-Lithium Nitrate have been redetermined in the region 20% to 30% Lithium Nitrate.

The vacuum drying method employed on all samples gave good,reproducible results in the region studied. It was found by analysis for nitrogen to produce close to 100% purity in a 48 hour period.

The eutectic temperature of Ammonium Nitrate 11 and Lithium Nitrate was found to be 90.4°C at a composition of 26.0% Lithium Nitrate.

APPENDIX I

THERMOMETER CALIBRATION

The thermometer was calibrated by comparison with the melting and boiling points of certain pure organic compounds. All melting point determinations were carried out in the melting point apparatus used in the cooling curve runs. On the basis of the results thus obtained a calibration curve was prepared by plotting the observed melting points of the standard compounds against the corrected values (Figure 4). By use of this curve all observed transition and eutectic temperatures were converted to correct values.

All boiling point measurements were carried out in a percolator boiling point apparatus[#7] and these measurements, without stem correction, were also plotted on the calibration curve.

TABLE 5.

THERMOMETER CALIBRATION DATA

SUBSTANCE	POINT	OBS. TEMP.	CORR.TEMP.
Ethyl alcohol	Boiling	78.40°C	78.26°C
Benzene	Boiling	80.05	80.00
Naphthalene	Melting	79.70	80.20
M-Dinitrobenzene	Melting	90.10	90.00
Steam	Condensing	100.10	100.00
Acetanilide	Melting	114.00	114.00
Benzoic acid	Melting	122.20	122.50

[#7] Shriner and Fuson, "Identification of Organic Compounds," Second Edition, John Wiley & Sons Inc., New York, N.Y., 1945, p.93.

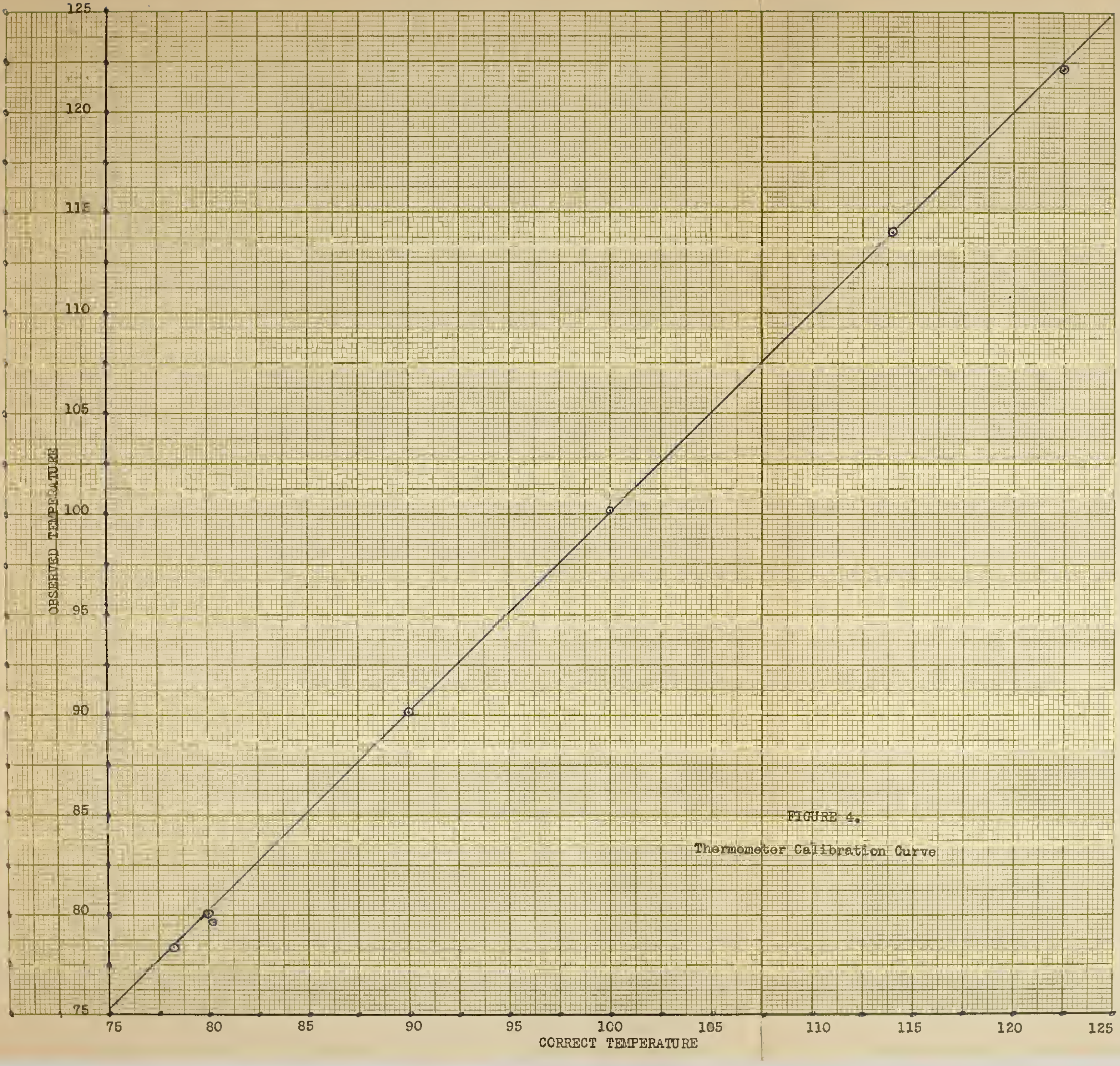

FIGURE 4.

Thermometer Calibration Curve

KEUFFEL & ESSER CO., N. Y. NO. [illegible]
10 x 10 to the 1/2 inch, 5th lines accented.
MADE IN U. S. A.

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